

Determining the Order of a Molecular Point Group

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Abstract

Conventional methods of identifying the point group of a molecule require skills in finding symmetry elements and operations. A useful aid to error checking is an ability to determine the order of a group purely from its label. To this end, Curnow has promulgated a set of simple empirical rules. In this article, Curnow's rules are substantiated using simple geometric considerations from the basis of point group generators. The proof is provided in a form that will be accessible to undergraduate chemistry students and their teachers.

Keywords: Symmetry, group theory, molecular structure

Introduction

Symmetry plays an important role in chemistry, particularly in respect to molecular structure, spectroscopy and crystallography. An elementary skill taught at the undergraduate level is identification of the symmetry elements of a molecule and the subsequent determination of its point group by using a decision-making flow diagram of the type found in many text books. A common problem with this process is that students are prone to missing whole classes of operations, particularly improper rotations (S_n) and C_2 operations in dihedral point groups; thus, for example, it is reasonable common for the chair form of cyclohexane to be misassigned to the C_6 or C_3 point group rather than to D_{3d} .

A useful exercise in helping students to refine their skills in identifying symmetry operations is to give them a picture of a molecule, along with the correctly assigned point group, and then require them to identify all operations without reference to a character table (where the operations would be listed). As a check for missing operations, it is clearly useful to be able to determine their total number – the order of the group – simply from the point-group label. To this end, Curnow gave three simple, empirical rules:(1)

1. Assign 1 for C or S, 2 for D, 12 for T, 24 for O, or 60 for I.
2. Multiply by n for any numerical subscript.
3. Multiply by 2 for any letter subscript label (s, v, d, h, i).

The veracity of Curnow's rules is readily established for a given point group, but it would obviously be better to have a general proof. In 1952, Weyl effectively provided such a proof as part of his demonstration that only certain point groups are permitted in three-dimensional space;(2) and more recently, a modified proof was presented by Kim.(3) Unfortunately, both Weyl's and Kim's proofs are of limited pedagogical utility in chemistry since they require levels of mathematics that are substantially in advance of what might normally be expected from an undergraduate chemistry student. Certainly, they are rather more abstract than would be ideal for presentation in an undergraduate chemistry text book.

This article presents a proof of Curnow's rules using simple geometric concepts and elementary group theory. Though perhaps less mathematically elegant than those presented by the earlier workers,(2, 3) it should be more accessible to both undergraduate chemistry students and their teachers, and therefore more appropriate for incorporation into chemistry text books.

Point-group Generators

The proof starts from the concept of group generators;(3) small, usually minimal or near-minimal,* subsets of symmetry operations from which all other operations of the group can be generated. Table 1 lists the molecular point groups (in a notation familiar to chemists) along with appropriate choice of group generators divided into two categories – principal and augmentory. For each group, G , one or two principal generators, α , define a principal subgroup, g_0 , of order h_0 . This is extended to the full group by the inclusion of N_β (up to two) further augmentory generators, β .

Except for the simplest groups (C_1 , C_2 , C_s and C_i) selection of generators is never unique and some of those listed in Table 1 are not minimal. For example, for C_{nh} point groups with odd values of n , S_{2n} could have been chosen as an unaugmented principal generator; for odd and even n , respectively, the D_{nh} and D_{nd} point groups can be generated by augmenting S_{2n} with just $C_2(\perp)$; for T_h and T_d , the principal generators could have been chosen as C_3 and C_2 , while selection of S_4 and C_3 for T_d would have required no augmentory generators. However the choices in Table 1 are convenient for this article in that: (a) they conform to common chemistry conventions for point group nomenclature; (b) they accord with the implied scheme of Curnow's rules; (c) they are efficient in the sense that the removal of any one generator would leave the group incomplete whereas inclusion of any other would lead to redundancies; and (d), important to the following derivation, the augmentory generators are all self-inverse ($\beta = \beta^{-1}$).

* A minimal set of group generators is the smallest subset required to completely define the point group. No molecular point group requires more than three group generators.

In terms of the parameters used in Table 1, Curnow's rules are more concisely expressed as

$$h = h_0 \times 2^{N_\beta} \quad (1)$$

The first step in validating this equation is the determination of h_0 . The second step is to show that the inclusion of N_β self-inverse augmentory generators expands the order by a factor of 2^{N_β} .

Table 1: Molecular point groups and their group generators^a

Point group G	Principal generator(s) α	h_0	Augmentory generator(s) β	N_β	Group order $h = h_0 \times 2^{N_\beta}$
C_n	C_n	n		0	n
C_{nv}	C_n	n	σ_v	1	$2n$
C_{nh}	C_n	n	σ_h	1	$2n$
S_n	S_n	n		0	n
D_n	C_n	n	$C_2(\perp)$	1	$2n$
D_{nd}	C_n	n	$C_2(\perp), \sigma_d$	2	$4n$
D_{nh}	C_n	n	$C_2(\perp), \sigma_h$	2	$4n$
T_d	$C_3(a), C_3(b)^{-1}$	12	σ_d	1	24
T_h	$C_3(a), C_3(b)^{-1}$	12	i	1	24
O_h	C_4, C_3	24	i	1	48
I_h	C_5, C_3	60	i	1	120

^a The non rotational groups are effectively included in this table as follows: $C_1 = C_{n=1}$; $C_\infty = C_{th}$ (or C_{1v}); $C_i = S_2$.

For the uniaxial cyclic (**C** and **S**) and dihedral (**D**) groups, a single principal generator, $\alpha = C_n$ or S_n , defines the principle subgroup, $g_0 = C_n$ or S_n .[§] The elements of g_0 are $\gamma_i = \alpha^i$ ($i = 1 \dots n$), where $\alpha^{n,j} = \gamma_{(j \bmod n)}$ and $\gamma_n = E$. Hence, $h_0 = n$ for these groups (third column of Table 1).

The situation is more complicated for the poly-axial, **T**, **O** and **I**, groups, which each have two principal generators. The principal subgroup for each of these groups comprises the rotational symmetry operations of a regular convex polyhedron (Platonic solid) composed of identical n -fold regular polygons, m of which meet at each vertex (Table 2). The shape of the polyhedron is defined by (n, m) . For example, a cube (Figure 1a) comprises six squares (4-fold polygons), three of which meet at each vertex, so $(n, m) = (4, 3)$; for a regular tetrahedron (Figure 1b), three equilateral triangles (3-fold polygons) meet at each vertex, so $(n, m) = (3, 3)$. Each rotational axis passes through the surface of the polyhedron at two antipodal symmetry points, which can be categorised as one of three types: vertices (filled circles in Figure 1), edge centres (open circles) and face centres (filled triangles or quadrilaterals). Each edge centre is associated with a C_2 axis and has another edge centre as its antipode (Figure 1). The symmetry operations C_n and C_m are, respectively, associated with the face centres and vertices, and constitute the principal generators listed in Table 1. When $n \neq m$ the two antipodal symmetry points of each principal generator must be of the same type, either both vertices or both face centres. This is illustrated for a cube in Figure 1a where the antipodes of the C_4 generator are both face centres while those for the C_3 generator are both

vertices. However, in the case of a tetrahedron, where $n = m = 3$, the antipode of a vertex is a face centre, and vice versa, as illustrated for the C_3 generator in Figure 1b.

Table 2: The principal sub groups of the poly-axial groups

g_0	Polyhedron	(n, m)	v_e	v_v	v_f	h_0
T	tetrahedron	(3, 3)	6	4	4	12
O	octahedron cube	(3, 4) (4, 3)	12 12	6 8	8 6	24
I	dodecahedron icosahedron	(5, 3) (3, 5)	30 30	20 12	12 20	60

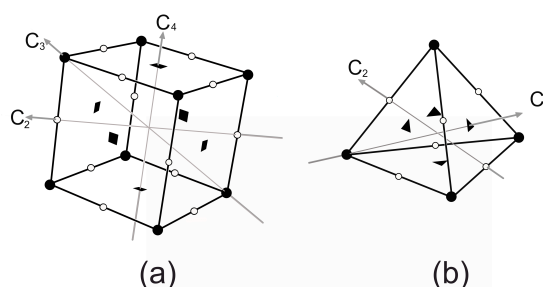


Figure 1. Examples of poly-axial figures showing rotation axes. Vertices are indicated by filled circles, edge centres by open circles and face centres by filled quadrilaterals or triangles. (a) A cube has $g_0 = O$ with $(n, m) = (4, 3)$: $v_e = 12$ edges, $v_v = 8$ vertices and $v_f = 6$ faces. (b) A regular tetrahedron has $g_0 = T$ with $(n, m) = (3, 3)$: $v_e = 6$ edges, $v_v = 4$ vertices and $v_f = 4$ faces.

The simplest way to determine h_0 is to count the symmetry operations of g_0 : there is a single identity plus $(k - 1)$ non-identity operations associated with the C_k axis passing through each pair of antipodal symmetry points. Thus,

$$h_0 = 1 + (v_e + v_v(m - 1) + v_f(n - 1))/2 \quad (2)$$

where v_e , v_v and v_f are, respectively, the numbers of edges, vertices and faces (Table 2). The numbers of symmetry points are interrelated by Euler's polyhedral formula;

$$v_f + v_v - v_e = 2 \quad (3)$$

Each face is an n -fold polygon with n edges, and each edge connects two faces, so

$$v_f = 2v_e/n \quad (4)$$

Each vertex is at the intersection of m edges and each edge connects two vertices, so

$$v_v = 2v_e/m \quad (5)$$

Simultaneous solution of equations 3 to 5 gives

$$v_e = 2nm/(2n + 2m - nm) \quad (6a)$$

$$v_v = 4n/(2n + 2m - nm) \quad (6b)$$

$$v_f = 4m/(2n + 2m - nm) \quad (6c)$$

Substituting equations 6a-c into equation 2 then gives

[§] For S_n and S_{2n} , only even values of n are permitted.

$$h_0 = 4nm/(2n + 2m - nm) \quad (7)$$

The consequent values of h_0 , listed in the right-most column of Table 2, are in accord with Curnow's rule number 1. Furthermore, equation 7 is symmetric with respect to the interchange of n and m , consistent with the fact that the symmetry is independent of the interchange of vertices and faces, for example when transforming a cube into an octahedron or a regular dodecahedron into an icosahedron.

Although \mathbf{g}_0 for all poly-axial groups contains C_2 operations, this is not explicit in equation 7, where h_0 depends only on the two principal generators (α_1 and α_2). Two (related) explanations can be offered for this. The first is that the number of C_2 operations is completely determined (via Euler's polyhedral formula – equation 3) by the numbers of C_n and C_m operations. The second is that the product of the two principal generators is a C_2 operation: $\alpha_1\alpha_2 = C_2$.

Determination of h

The inclusion of each self-inverse augmentor doubles the order of the group, as follows. If the operations of \mathbf{g}_0 are $\gamma_1, \gamma_2 \dots \gamma_{h_0}$, then the inclusion of β results in h_0 new operations that can be represented as products of the type

$$\gamma_{h_0+i} = \beta \gamma_i \quad (i = 1 \dots h_0) \quad (8)$$

(the right-hand side of which is to be read as application of operation γ_i followed by operation β). In fact, equation 8 represents *all* possible new operations, as can be demonstrated via the group-theoretical concept of similarity. For any arbitrary symmetry operation ϕ that belongs to \mathbf{G} , the product $\phi^{-1}\gamma_j\phi$ is "similar" to (belongs to the same class as) γ_j ; and if γ_j belongs to \mathbf{g}_0 then so must $\phi^{-1}\gamma_j\phi$. Consequently, since β is a self-inverse member of \mathbf{G} ,

$$\beta \gamma_j \beta = \gamma_j \in \mathbf{g}_0 \quad (9)$$

Pre-multiplying equation 9 by β gives

$$\gamma_j \beta = \beta \gamma_i \quad (10)$$

Thus, every product in which β is a pre-multiplier (first operation) is identical to a product already included by equation 8 where β is a post-multiplier (second operation). The same argument applies for the inclusion of each of the N_β augmentory generators in the sequence

of subgroups between \mathbf{g}_0 and \mathbf{G} . Hence equation 1 is established and Curnow's rules are vindicated.

Summary

Curnow's rules for determining the order of a point group from its label can be considered as a product of two parts, as expressed by equation 1: the order (h_0) of a principal subgroup that is defined by the principal group generators; and a doubling of that order by the inclusion of each of up to two self-inverse augmentory generators. This result is affirmed by simple geometric considerations and elementary group theory.

As an interesting aside, equations 4-7 give the results that $2\nu_e = m\nu_v = n\nu_f = h_0$. In an early step of Weyl's demonstration that the only possible proper (rotation-only) groups with less than spherical symmetry are \mathbf{C}_n , \mathbf{D}_n , \mathbf{T} , \mathbf{O} and \mathbf{I}_h , (2) he showed, quite generally for any polyhedron, that

$$k\nu_\kappa = N \quad (11)$$

In equation 11, N is the total number of proper rotational operations (including the identity) of the polyhedron, κ is one of the (up to two) types of symmetry points through which the C_k axis passes and ν_κ is the total number of points of type κ . After combining equation 11 with a more general form of equation 2 for any polyhedron with two or more rotational symmetry axes, he derived the equation

$$1 + 2/N = 1/n + 1/m + 1/2 \quad (12)$$

Setting $N = h_0$, equation 12 is simply rearranged to give equation 7. Setting $m = 2$ and $N = h$ gives the (correct) result of $h = 2n$ for the \mathbf{D}_n point groups.

Acknowledgement

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References

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